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# Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools

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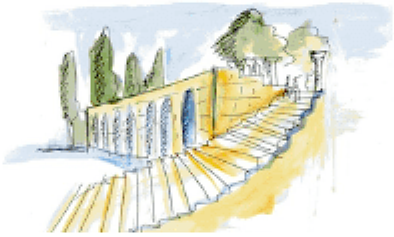



## ORAL 33

# EFFECT OF UV TREATMENT ON DBPS FORMATION IN CHLORINATED SEAWATER SWIMMING POOLS- A LABORATORY STUDY


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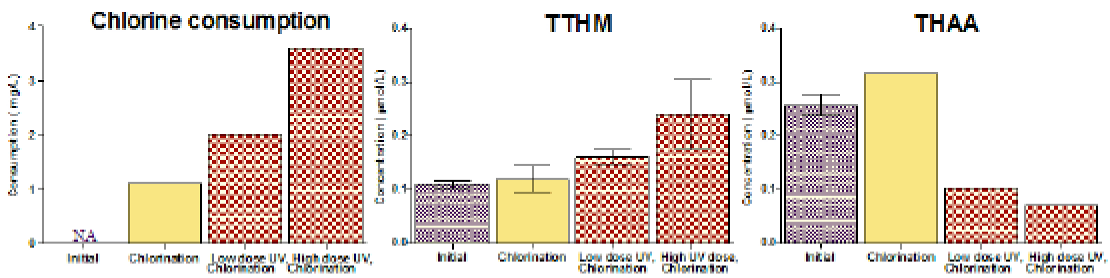
### Highlights

- UV treatment increased the reactivity of seawater pool water towards chlorine
- UV treatment reduces haloacetic acid concentrations after re-chlorination
- Post-UV chlorination increases trihalomethane and haloacetonitrile concentrations
- Increase in concentrations predicts higher toxicity after single UV treatment and chlorination

### Graphical abstract




### Aims

The aim of this study was to investigate the effect of UV treatment followed by chlorination on DBP formation was studied using laboratory experiments. Three groups of DBPs were investigated including THMs, HANs and HAAs. DBP level measured after post-UV chlorination was compared to dark control sample which was not subjected to UV exposure. Bromine substitution was investigated to analyse its effects on the formation of DBPs. Finally, overall cytotoxicity and genotoxicity were estimated for the toxic potency of compounds before and after treatment.

### Methods

UV treatment

Batch experiments were conducted by using a thermostatic controlled cylindrical reactor with a standard medium-pressure UV lamp (P=700 W, Peschl Ultraviolet). In this work, UV dose was determined according to method described by Hansen et al. [1]. UV exposure cylindrical reactor setup was correlated to the real flow through system on the pool by using combined chlorine as an actinometer. UV system needs 1.0 kWh/m$^3$ to remove 90% of combined chlorine and 0.61 kWh/m$^3$ to remove monochloramine [1]. The required radiation time for the cylindrical reactor setup to remove 90% of the monochloramine from the pool sample was 4.2 min (2.1 $J/cm^2$).

Chlorination

The formation of DBPs as a result of chlorination was investigated using a standardised DBP formation assay. The concentration of free chlorine was adjusted to 3.0 ± 0.05 mg/L by adding sodium hypochlorite solution and then the sample reacted for 24 h at 25 °C. Chlorination was performed in quadruplicate, with three samples used for DBP analysis and two for the determination of residual chlorine. Samples for DBP analyses were dosed with ammonium chloride solution (50 mg/L), to quench free chlorine which neither affects the already formed DBP [2] nor increases N-DBP formation [3]. The samples were extracted and analysed for DBPs the same day.

## Results

Chlorine consumption increased with post-UV chlorination likely because UV irradiation degraded organic matter in the pool samples to more chlorine reactive species. Haloacetic acids (HAA) concentrations decreased significantly due to photodegradation. However, concentration of trihalomethanes (THM) and haloacetonitriles (HAN) increased with post-UV chlorination. Bromine incorporation in HAA was significantly higher in control samples chlorinated without UV irradiation but decreased significantly with UV treatment. Bromine incorporation was promoted in THM and HAN after UV and chlorine treatment. Overall, the accumulated bromine incorporation level in DBPs remained essentially unchanged in comparison with control samples after post-UV chlorination. Toxicity estimates increased with single dose UV and chlorination mainly due to the increased HAN concentrations. However, brominated HANs are known in literature to be degraded with further UV treatment.

## Conclusions

The present study is the first to investigate the fate of brominated DBPs submitted to medium-pressure UV lamp followed by post-chlorination, on real seawater swimming pool samples. Firstly, UV treatment is an efficient method to decrease the combined chlorine level in swimming pools. However in seawater pools, UV treatment has a potential to photodegrade the DBP as brominated DBPs are easier photolysed than the chlorinated ones [1]. The results obtained in this study show that the UV treatment followed by chlorination does not lead to real abatement in DBP content. Only levels of dibromoacetic acid and dibromochloroacetic acid were significantly lowered, whereas levels of bromoform, dibromochloromethane, bromochloroacetonitrile and dibromoacetonitrile increased. These findings have also to be correlated to the observed increase in estimated cytotoxicity and genotoxicity in the whole real samples submitted to UV treatment followed by chlorination. This increase in toxicity can be attributed to increase of levels of DBPs, and especially of HAN [4]. This study raises thus the issue that UV used for combined chlorine reduction could result in increased formation of some of brominated DBPs in seawater swimming pools. However, further studies are still needed to interpret present findings, including influences of composition of water, UV dose rate, UV wavelength and, chlorine dose on the kinetics of brominated DBP formation or disappearance.

## References


1. K. M. S. Hansen, R. Zortea, A. Piketty, S. R. Vega, and H. R. Andersen, "Photolytic removal of DBPs by medium pressure UV in swimming pool water.," *Sci. Total Environ.*, vol. 443, pp. 850–856, Jan. 2013.
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Technical University of Denmark

# Effect of UV treatment on formation of disinfection by-products in chlorinated seawater swimming pools

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**DTU Environment**
Department of Environmental Engineering

# Seawater Pools
## Brominated DBPs

Composition of seawater (mg/L)

Source: Water Condition & purification, 2005

| | Typical Seawater | Eastern Mediterranean | Arabian Gulf at Kuwait | Red Sea at Jeddah |
|---|---|---|---|---|
| Chloride ($Cl^-$) | 18.980 | 21.200 | 23.000 | 22.219 |
| Sodium ($Na^+$) | 10.556 | 11.800 | 15.850 | 14.255 |
| Sulfate ($SO_4^{2-}$) | 2.649 | 2.950 | 3.200 | 3.078 |
| Magnesium ($Mg^{2+}$) | 1.262 | 1.403 | 1.765 | 742 |
| Calcium ($Ca^{2+}$) | 400 | 423 | 500 | 225 |
| Potassium ($K^+$) | 380 | 463 | 460 | 210 |
| Bicarbonate($HCO_3^-$) | 140 | - | 142 | 146 |
| Strontium ($Sr^{2+}$) | 13 | - | - | - |
| Bromide ($Br^-$) | 65 | 155 | 80 | 72 |
| Borate ($BO_3^{3-}$) | 26 | 72 | - | - |
| **Total dissolved solids (TDS)** | **34.483** | **38.600** | **45.000** | **41.000** |

Skin conditions & wounds

Hay fever & sinus issues

**Meditation & relaxation**

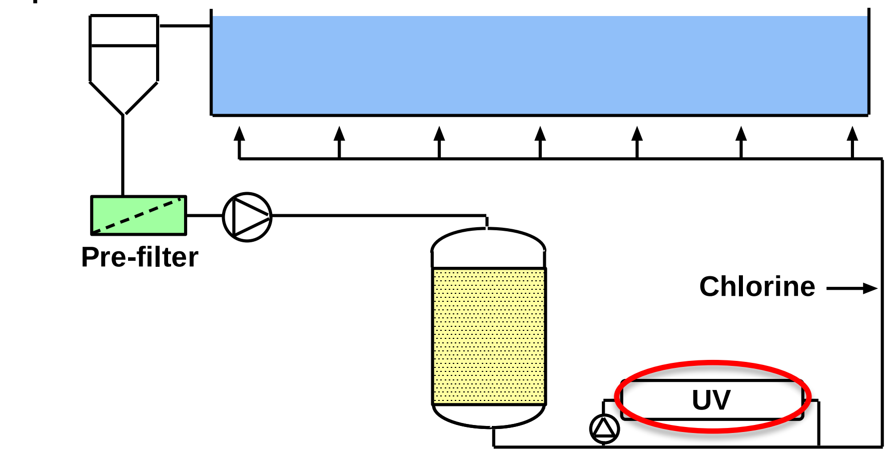
$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

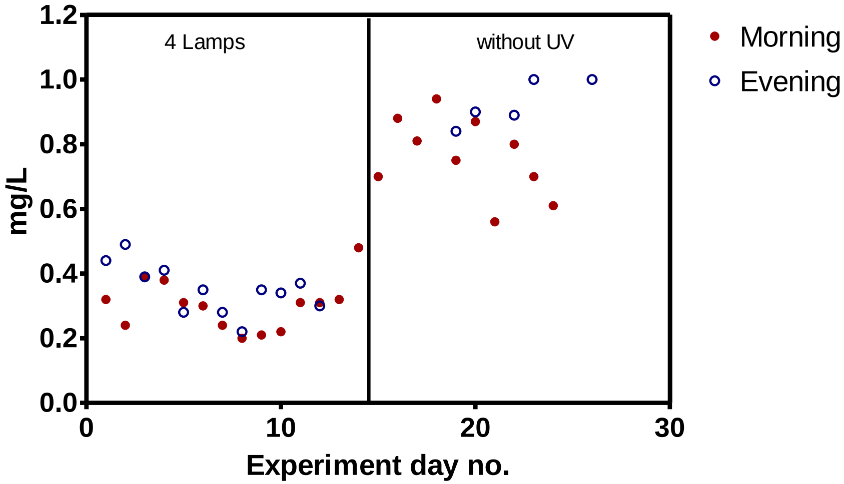
$$HOBr + DM \rightarrow Br\text{-}DBPs$$

Seawater pools disinfection resulted in brominated DBPs


ATLANTIC OCEAN
FRANCE
SLOVENIA
CROATIA
ITALY
Ligurian Sea
Gulf of Lion
Corsica
Adriatic Sea
Bla
Bosphorus
Strait of Otranto
ALBANIA
Tyrrhenian Sea
Sardinia
SPAIN
PORTUGAL
Balearic Sea
Balearic Islands
Thracian Sea
Sea of Marmara
Dardanelles
GREECE
TURKEY
Aegean Sea
MEDITERRANEAN
Sicily
Ionian Sea
Strait of Messina
Sea of Sicily
Myrtoan Sea
Strait of Gibraltar
Alboran Sea
SEA
MALTA
Sea of Crete
Crete
Gulf of Antalya
Cyprus
Gulf of Gabès
ALGERIA
Libyan Sea
Levantine Sea
TUNISIA
MOROCCO
Gulf of Sidra
LIBYA
EGYPT

# UV Treatment
## Chloramine removal

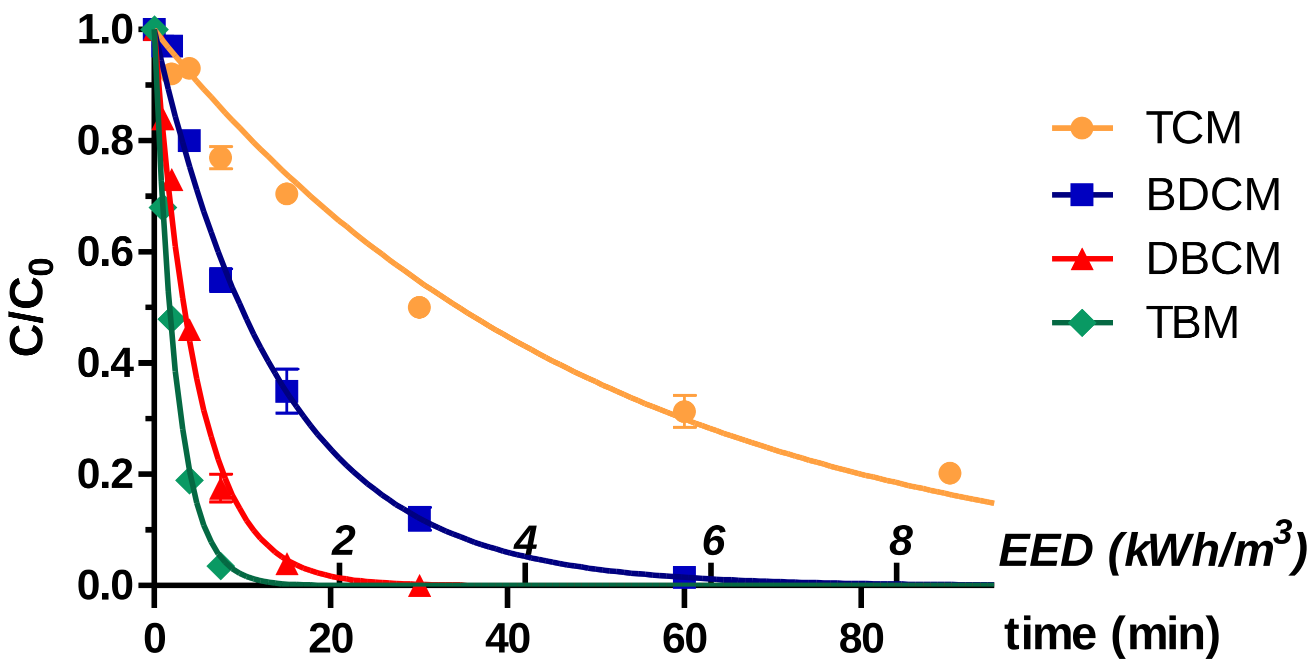



- UV treatment followed by $Cl_2$ → decreased combined $Cl_2$

Kristensen et al., 2010, Report, Ministry of the Environment

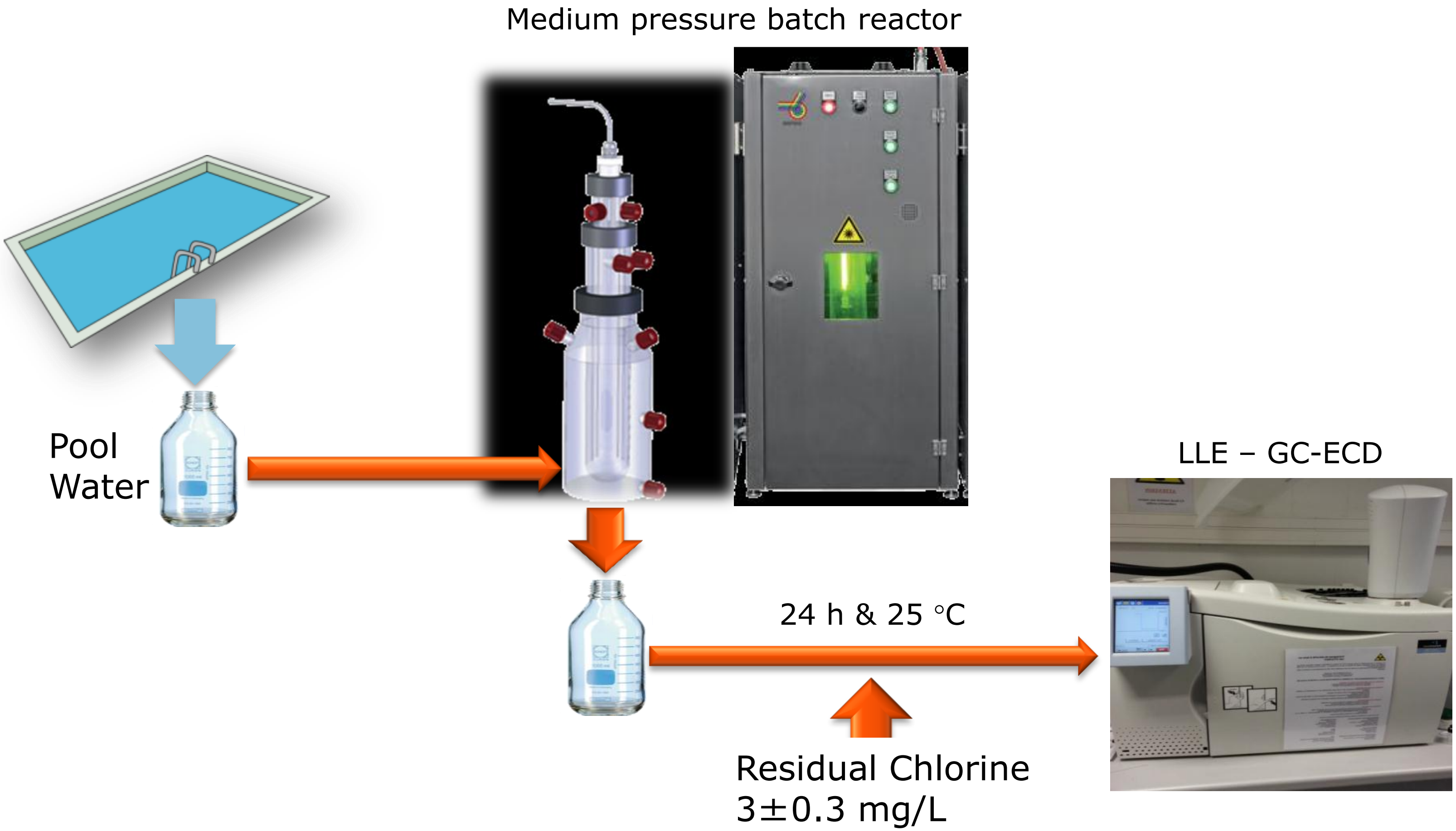
# UV Treatment
## By-product photolysis




- Increased bromine substitution → increasing removal

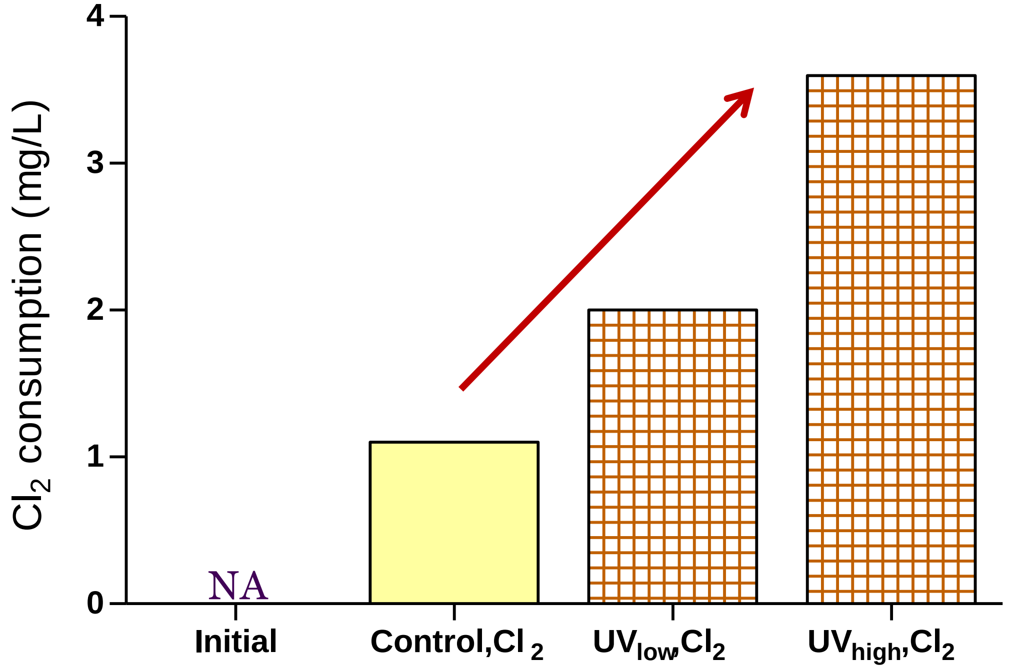
Hansen et al., Science of the Total Environment, 443, pp. 850

# UV Treatment
## Experimental setup



# Results

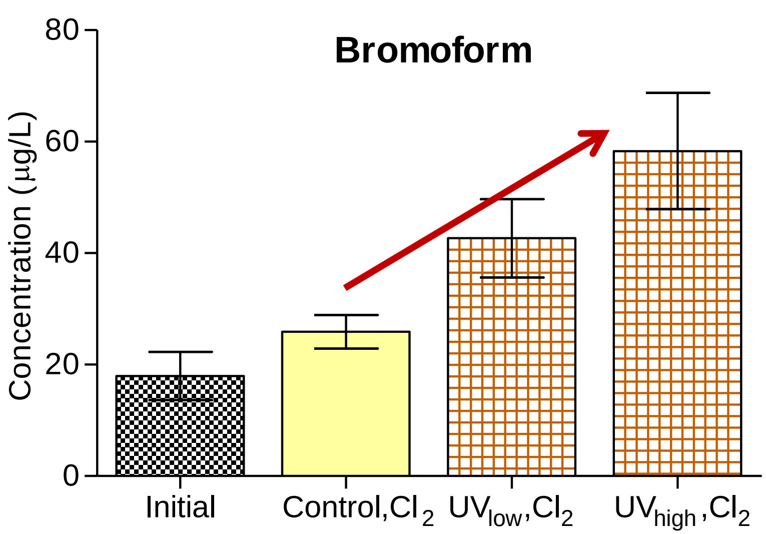
## $CL_2$ consumption

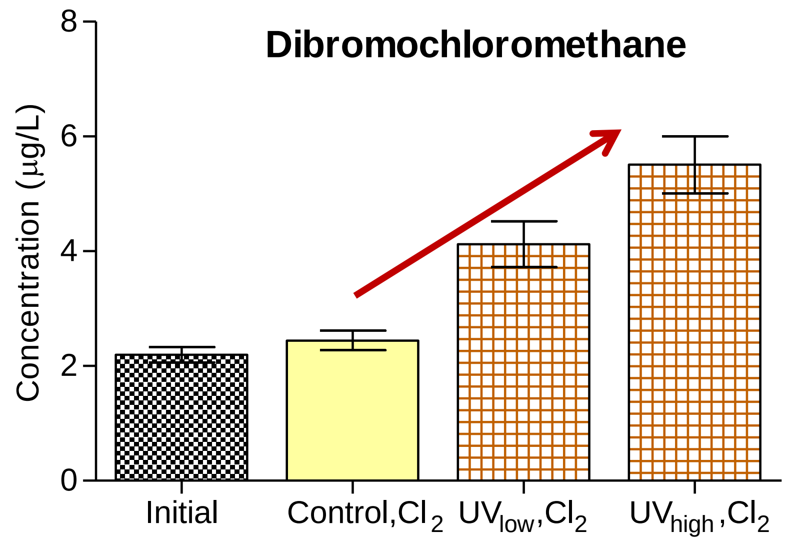



- Low UV dose followed by $Cl_2$ → low increase in $Cl_2$ reactivity
- High UV dose followed by $Cl_2$ → high increase in $Cl_2$ reactivity

Cheema et al., 2017, Effect of medium-pressure UV-lamp treatment on DBPs in chlorinated seawater swimming pool waters, STOTEN.

# Results
## Trihalomethanes

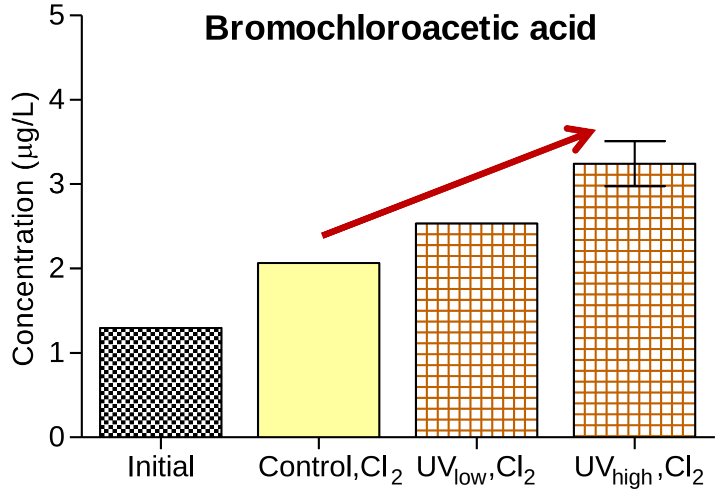


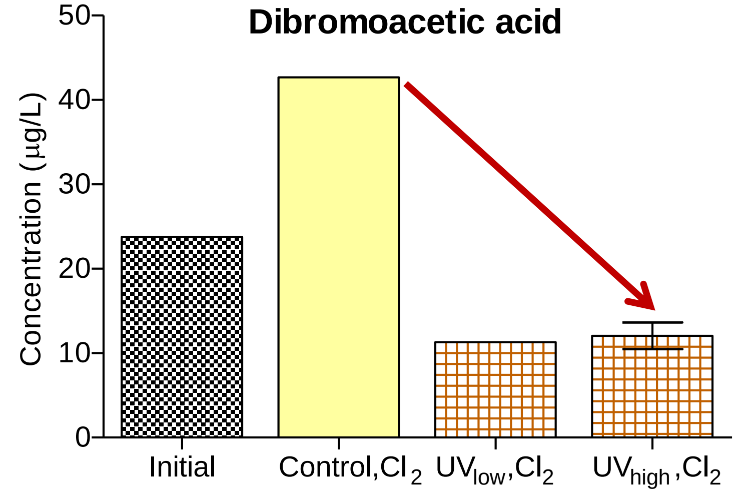



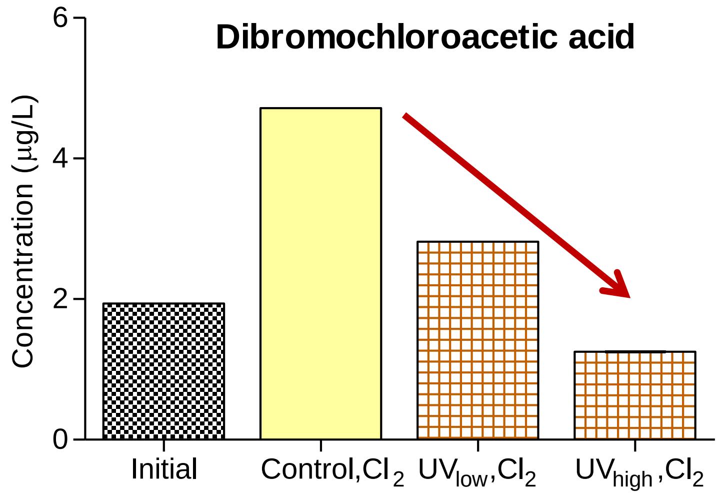

- UV treatment followed by $Cl_2$ → increased Bromoform
- UV treatment followed by $Cl_2$ → increased Dibromochloromethane

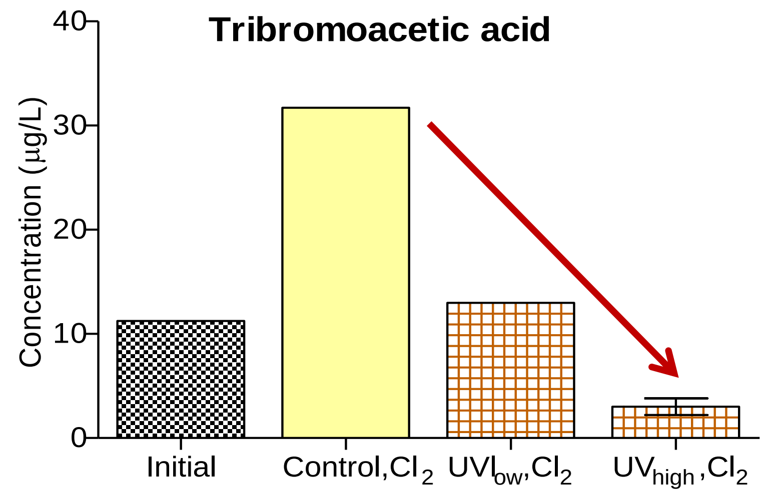
Cheema et al., 2017, Effect of medium-pressure UV-lamp treatment on DBPs in chlorinated seawater swimming pool waters, STOTEN.

# Results
## Haloacetic Acids

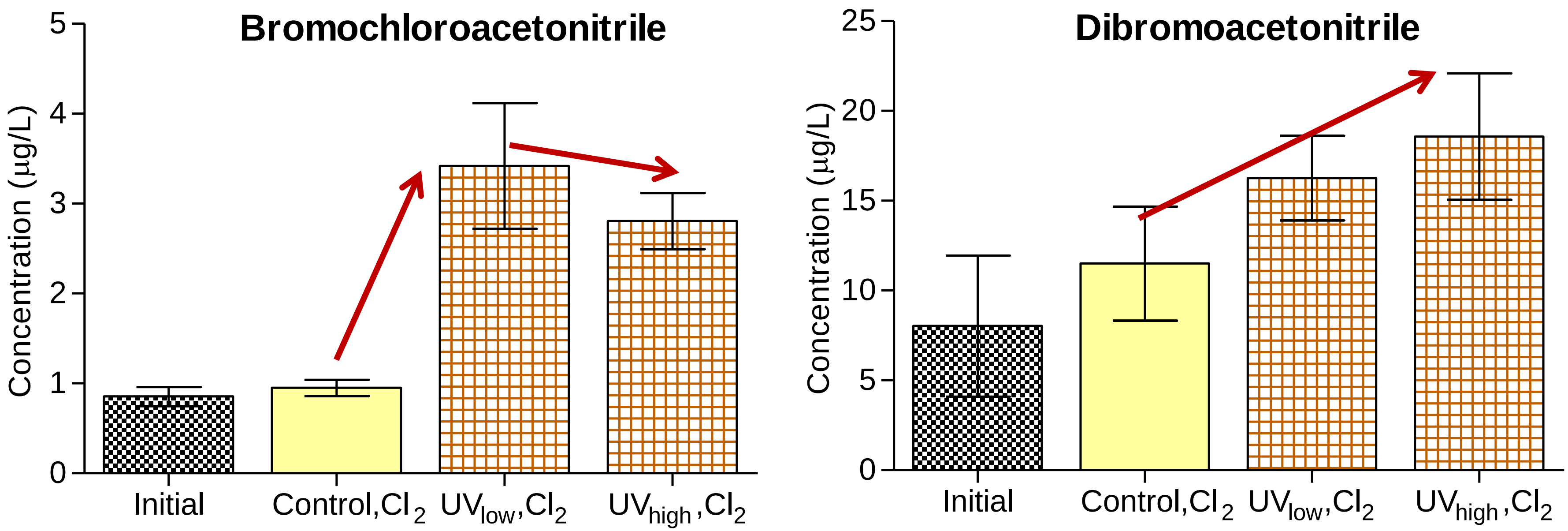


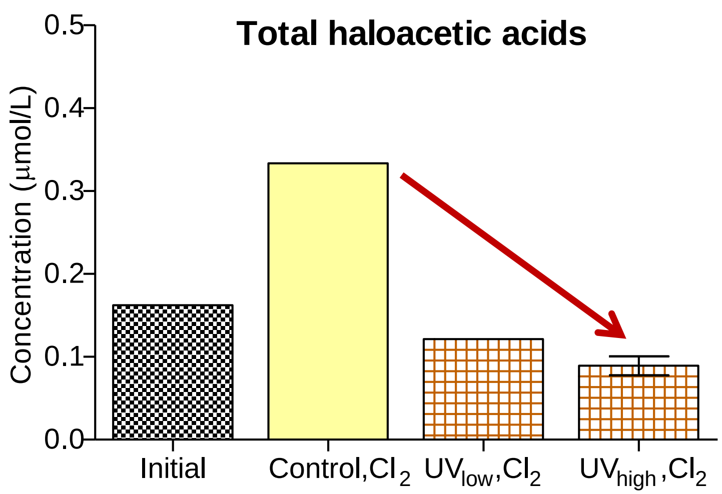
# Results
## Haloacetonitriles

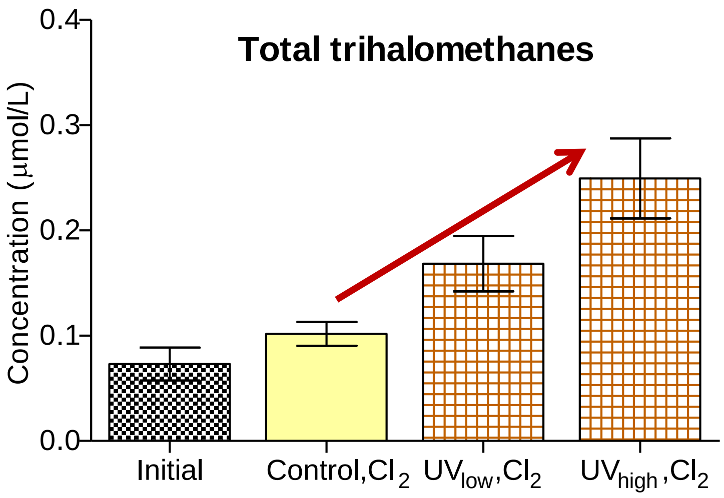


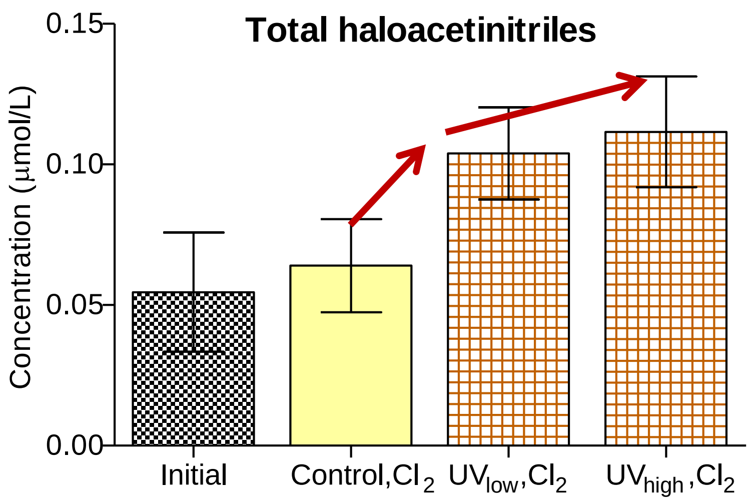

- UV treatment followed by $Cl_2$ → increased Bromochloroacetonitrile
- UV treatment followed by $Cl_2$ → increased Dibromoacetonitrile

Cheema et al., 2017, Effect of medium-pressure UV-lamp treatment on DBPs in chlorinated seawater swimming pool waters, STOTEN.

# Results
## Summary



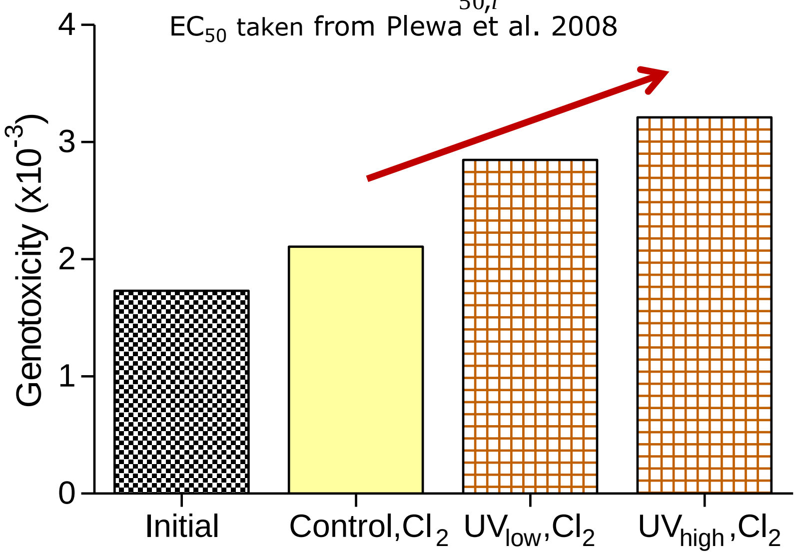

- UV treatment followed by $Cl_2$ → decreased Total HAA
- UV treatment followed by $Cl_2$ → increased Total THM
- UV treatment followed by $Cl_2$ → increased Total HAN

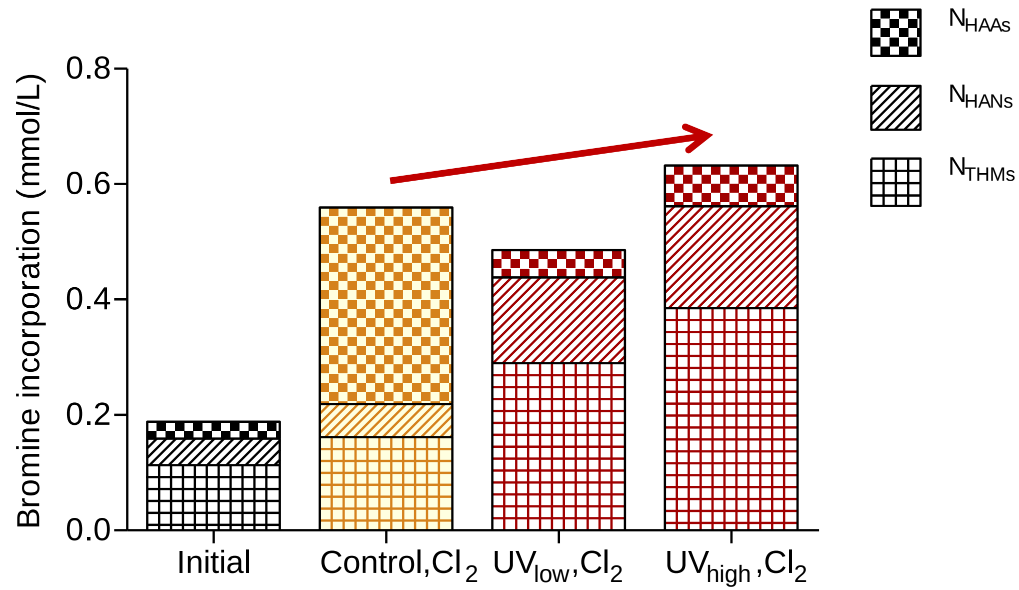
Cheema et al., 2017, Effect of medium-pressure UV-lamp treatment on DBPs in chlorinated seawater swimming pool waters, STOTEN.

# Predicted toxicity & Bromine incorporation

$$Toxicity = \sum \frac{C_i}{EC_{50,i}}$$

$EC_{50}$ taken from Plewa et al. 2008




- Single UV treatment followed by $Cl_2$ → increased toxicity
- Single UV treatment followed by $Cl_2$ → Bromine incorporation unchanged



Cheema et al., 2017, Effect of medium-pressure UV-lamp treatment on DBPs in chlorinated seawater swimming pool waters, STOTEN.

# Thanks for your attention!